

Surface Segregation in Polymer Blends and Interpolymer Complexes with Increasing Hydrogen Bonding Interactions

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ABSTRACT: The evolution of surface composition in polymer blends and interpolymer complexes was studied using X-ray photoelectron spectroscopy (XPS) and Time-of-Flight secondary ion mass spectroscopy (ToF-SIMS). For immiscible and miscible poly(styrene-co-4-vinyl phenol)/poly(styrene-co-4-vinyl pyridine) (STVPh/STVPy) blends, surface enrichment by the lower surface energy component STVPh was always observed. Increasing VPh contents in STVPh from 0 to 16 mol % spans the transition from immiscible to miscible blends; the differences in surface free energies between STVPh and STVPy decreased, but surface enrichment of STVPh continued to increase. This is due to the strong hydrogen bonded self-association of STVPh, which dominates over the immiscibility to miscibility transition in controlling the surface composition. In the immiscible and miscible blends, decreasing the molecular weights of STVPy, which decreased the surface free energy of STVPy, systematically reduced surface enrichment by STVPh. For STVPh/STVPy complexes formed at VPh contents higher than 21 mol %, surface enrichment of STVPh is barely detectable. STVPh and STVPy form a new supramolecular species. Interpolymer complexation is now the decisive factor controlling the surface composition, dominating over the surface free energy differences; the effect of STVPy molecular weight variation on the surface composition is also negligible for the interpolymer complexes. ©2005 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 43: 1924–1930, 2005

INTRODUCTION

The macroscopic behavior of polymer blends near surfaces differs from that in the bulk and has recently been the subject of many interest-

ing studies because of the control exerted by the surface composition on a variety of technologically important properties of blends.^{1–5} In most cases, the surface of a two-phase polymer mixture should consist predominately of one component with lower surface free energy, since thermodynamics already favor complete demixing.^{6,7} In miscible blends, lower surface energies may

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also be achieved by preferential placement of one component at the surface.^{2,8,9}

In principle, the surface composition of polymer blends has been found to depend strongly on the differences between the interactions of the two species with the surface, that is, the relative surface free energy; it also depends on the magnitude of the interactions between the two polymer constituents, which determines their degree of miscibility.^{10–16} Although surface segregation in polymer blends has been extensively studied, experimental work concerning surface enrichment in blends with specific interactions, such as hydrogen bonding, has received less attention.^{17–25} Cowie and coworkers^{9,17} studied modified polystyrene/poly(vinyl methyl ether) blends with intermolecular hydrogen-bonding interactions using Fourier transform infrared attenuated total reflectance (FTIR-ATR). The limitation of this method is that it is not surface-sensitive enough (about 1 μm in detection depth). Duan and coworkers¹⁸ recently reported that surface enrichment in miscible polymer blends is partially reduced due to hydrogen bonding interactions between component polymers. Goh and colleagues^{21–23} have concentrated on surface characterization of polymer blends and interpolymer complexes. Generally, for an immiscible blend, low surface energies can be easily obtained because of the weak interaction between the blend components. However, for blends involving hydrogen bonding interactions, the hydrogen bonding interactions between component polymers makes the surface segregation more difficult. For interpolymer complexes, we have previously reported that the surface segregation can be almost eliminated,²⁵ but this conclusion cannot be generalized before more systems are carefully checked.

We introduce controllable hydrogen bonding interactions into component polymers, that is, poly(styrene-*co*-4-vinyl phenol)/poly(styrene-*co*-4-vinyl pyridine) (STVPh/STVPy) blends; by increasing the density of hydrogen bonding interaction groups, the blends can vary from immiscible to miscible blends and finally to interpolymer complexes. In the complexes, the two polymers form precipitates upon mixing the two component polymer solutions in a common solvent. STVPh has strong hydrogen bonded self-association, compared to another proton-donating polymer—poly(styrene-*cop*-hexafluoro-hydroxy-isopropyl- α -methyl styrene—which is reported in our previous paper.²⁵ How will this affect the surface segregation in immiscible, miscible, and interpolymer complexes is an

interesting issue. In this article, we systematically studied the effect of bulk mixing thermodynamics, surface energy differences, and self-association of component polymers on the surface enrichment of polymer blends and interpolymer complexes using X-ray photoelectron spectroscopy (XPS) and Time-of-Flight secondary ion mass spectroscopy (ToF-SIMS).

EXPERIMENTAL

Materials

Poly(styrene-*co*-4-vinyl phenol) (STVPh) copolymers were synthesized by bulk copolymerization of styrene and 4-acetoxystyrene at 60 °C using AIBN as initiator, followed by hydrolysis with hydrazine hydrate in 1,4-dioxane.²⁶ The molecular weights, polydispersity, and VPh contents in STVPh random copolymers was determined by size exclusion chromatography (SEC) and ¹H NMR from the precursor - poly(styrene-*co*-4-acetoxystyrene). The final products were purified by precipitation from THF to *n*-hexane three times. Poly(styrene-*co*-4-vinyl pyridine) (STVPy) copolymers were synthesized as previously described.²⁴ The molecular weights of STVPy copolymers were adjusted by altering reaction temperature and the amount of initiator (AIBN). The molar contents of 4-vinyl pyridine (VPy) were determined from nitrogen measurements. The number-average molecular weights and polydispersities of STVPy copolymers were determined by SEC. Table 1 lists the physical properties of STVPh and STVPy copolymers. STVPy-74 copolymers with 3 different molecular weights

Table 1. The Characteristic Data of STVPh and STVPy Samples Used in This Study

Sample Code	VPh or VPy Contents		$M_n/10^3$	M_w/M_n	T_g (°C)
	(mol %)				
PS	0		116	1.03	101
STVPh-3	3		90	1.60	106
STVPh-9	9		102	1.52	113
STVPh-16	16		117	1.50	121
STVPh-21	21		115	1.55	125
STVPh-48	48		144	1.52	140
STVPh-76	76		203	1.67	163
STVPy-74- <i>h</i>	74		109	1.68	146
STVPy-74- <i>m</i>	74		40	1.51	144
STVPy-74- <i>l</i>	74		10	1.65	140

from high to low are denoted as STVPh-74-*h*, STVPh-74-*m*, and STVPh-74-*l*, respectively. Polystyrene prepared by anionic polymerization was also used in this study.

Sample Preparation

STVPh copolymers and STVPh-74 with different molecular weights were separately dissolved in THF at a concentration of 15 g/L. A blend solution was prepared by mixing the same amount of each polymer solution under stirring. Depending on the VPh contents in STVPh, the mixed solutions might remain clear or form interpolymer complex precipitate. For PS/STVPh-74, STVPh-3/STVPh-74, STVPh-9/STVPh-74, and STVPh-16/STVPh-74, the clear solutions were spin-cast at 3800 rpm onto silicon wafers. The film thickness was kept at about 200–230 nm. When the VPh content in STVPh is higher than 21 mol %, the blend solutions form precipitates due to interpolymer complexation. The precipitates were separated by centrifugation, washed with THF three times, and then kept in THF. The bulk compositions of the complex precipitates were determined from nitrogen elemental analysis. The slightly swelled precipitates were pressed onto a silicon wafer to form thin and smooth films. All the films were dried under vacuum at room temperature overnight, then heated to and kept at 180 °C for 40 mins, followed by slow cooling at a rate of 0.5 °C/min to room temperature under vacuum.

Differential Scanning Calorimetry

DSC measurements were conducted with a differential scanning calorimeter (DSC-50, Shimadzu). The heating rate was 10 °C/min, and samples of about 10 mg in a sealed alumina cell were measured under a nitrogen gas atmosphere. The samples were heated to and kept at 180 °C for 15 min, followed by cooling to 25 °C at a rate of 1 °C/min.

Surface Characterization

The surface chemical composition and the binding energy were obtained from XPS. The XPS spectra were obtained with a PHI 5600 multi-technique system equipped with a monochromatic Al K α X-ray source. A pass energy of 23.4 eV was used. All core-level spectra were referenced to the C 1s neutral carbon peak at

285.0 eV. The emission angle (the angle between the surface normal and the axis of the analyzer) of the photoelectron was 45°, corresponding to a sampling depth of approximately 47 Å.^{27,28} For the XPS peak fittings, STVPh-16/STVPh-74 blends have very low STVPh surface concentration, so the N1s signal is very weak; the fitting error deduced from peak fitting software is about $\pm 10\%$. For other N1s and O1s peak fittings, typical overall fitting errors are about $\pm 3\%$.

ToF-SIMS measurements were performed on a Physical Electronics PHI 7200 ToF-SIMS spectrometer. The primary ions were generated from a Cs ion source (8 kV). The scanned area was 200 $\mu\text{m} \times 200 \mu\text{m}$, and the total ion dose for each spectrum acquisition was $< 4 \times 10^{12}$ ions/cm². Charge compensation was realized by low-energy (0–70 eV) flooding electrons being pulsed out of phase of the primary ion beam.

RESULTS AND DISCUSSION

Bulk Miscibility of STVPh/STVPh Blends and Complexes

The glass transition temperatures of STVPh/STVPh blends with different VPh contents in STVPh are shown in Table 2. PS/STVPh-74-*h* and STVPh-3/STVPh-74-*h* blends are immiscible, showing two distinct T_g's. STVPh-9/STVPh-74-*h* blends are miscible, which show only one T_g, indicating bulk miscibility on the length scale of at least 20–40 nm. When VPh contents in STVPh are higher than 21 mol %, STVPh and STVPh-74-*h* form interpolymer complexes that separated out from the solution as precipitates, which certainly show one T_g. The T_g values of the interpolymer complexes are much higher than T_g values calculated from the Fox equation. The higher the VPh contents, the larger the differences between the measured and calculated T_g, indicating that in the STVPh/STVPh complexes, the mobility of individual chains is greatly reduced as a result of the strong hydrogen bonding interaction between STVPh and STVPh.^{29,30} The molecular weight of STVPh has little effect on the bulk miscibility of STVPh/STVPh blends and the formation of interpolymer complexes.

Hydrogen Bonding Interactions Between STVPh and STVPh Evidenced by XPS

Figure 1 shows the N 1s core-level spectra of STVPh-74-*h* and STVPh-3, 9, 16, 21, 76/STVPh-

Table 2. Characteristic Data of STVPh/STVPy Blends or Complexes

Sample Code	Bulk Composition (STVPh, mol %)	T_g ($^{\circ}\text{C}$)	Surface Concentration (STVPh, mol %)	Surface Excess of STVPh (mol %)
PS/STVPy-74- <i>h</i> ^a	50 ^a	102/146	78 ^a	28 ^a
STVPh-3/STVPy-74- <i>h</i>	50	112/146	85	35
STVPh-3/STVPy-74- <i>m</i>	50	113/145	82	32
STVPh-3/STVPy-74- <i>l</i>	50	114/145	48	-2
STVPh-9/STVPy-74- <i>h</i>	50	134	92	42
STVPh-9/STVPy-74- <i>m</i>	50	133	87	37
STVPh-9/STVPy-74- <i>l</i>	50	133	79	29
STVPh-16/STVPy-74- <i>h</i>	50	141	94	44
STVPh-21/STVPy-74- <i>h</i>	59	151	63	4
STVPh-48/STVPy-74- <i>h</i>	62	160	64	2
STVPh-48/STVPy-74- <i>l</i>	62	157	63	1
STVPh-76/STVPy-74- <i>h</i>	60	174	61	1

^a Pure PS sample is used as a control; the bulk, surface concentration, and surface excess is calculated based on PS.

74-*h* blends or complexes. The N 1s spectrum of STVPy-74-*h* shows a single nitrogen environment with a binding energy (BE) of 399.0 eV. The N 1s spectrum of immiscible STVPh-3/STVPy-74-*h* is nearly the same as that of pure PVPy. When the VPh content reaches 9 mol %, the N 1s peaks of the blends are shifted slightly to the higher-BE ends, indicating that the nitrogen in the blends becomes slightly more electropositive due to hydrogen bonding interactions. The N 1s peak of the STVPh/STVPy-74-*h* blends with VPh contents higher than 9 mol % can be clearly deconvoluted into two component peaks: one remains at 399.0 eV and the other is at around 399.9 eV. This indicates that there was no proton transfer between hydroxyl and pyridyl, since for positively charged pyridinium ions, the higher-BE peak should be located at around 401.5 eV.³¹ For immiscible STVPh-3/STVPy-74-*h* blends, STVPh

and STVPy will phase separate into isolated domains on the surface, so hydrogen bonding interactions between hydroxyl and pyridyl groups can only take place at the interface. Its N 1s spectrum shows little difference from that of pure PVPy. When the VPh content in STVPh was increased further, it was found that the fraction of high-BE peak in the total N 1s spectrum increased considerably, indicating that more pyridyl groups in STVPy are now hydrogen bonded to hydroxyl groups in STVPh.

Figure 2 shows the O 1s core-level spectra of STVPh-21 and five STVPh/STVPy blends with different VPh contents. The O 1s electron of STVPh has a binding energy value of ca. 533.2 eV. This value is much lower than our previously reported O 1s binding energy (534.2 eV) in poly(styrene-*cop*-hexafluorohydroxy- isopropyl-*α*-

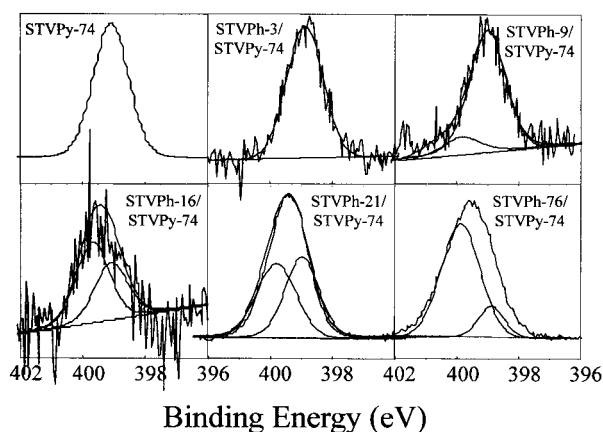


Figure 1. XPS N 1s core-level spectra of STVPy-74-*h* and STVPh-3, 9, 16, 21, 76/STVPy-74 blends or complexes.

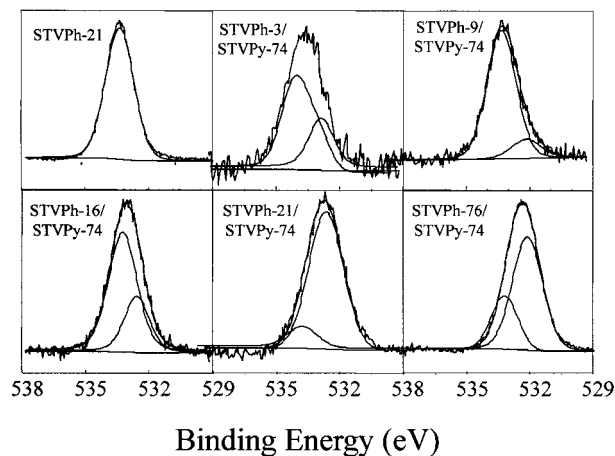


Figure 2. XPS O 1s core-level spectra of STVPh-21 and STVPh-3, 9, 16, 21, 76/STVPy-74-*h* blends or complexes.

Table 3. XPS Curve Fitting Results of STVPh/STVPy-74-*h* Blends or Complexes

Blends or Complexes Samples	Surface Concentration of STVPh (mol %)	Fraction of		N 1s BE	Fraction of High BE N1s Peak
		O 1s BE	Low BE O 1s Peak		
PS/STVPy-74	78	/	/	399.0	/
STVPh-3/STVPy-74	85	531.9/533.2	0.08	399.0/399.9	0.02
STVPh-9/STVPy-74	92	532.1/533.2	0.13	398.9/399.9	0.16
STVPh-16/STVPy-74	94	532.1/533.3	0.17	399.0/399.9	0.58
STVPh-21/STVPy-74	63	532.0/533.3	0.90	399.0/399.9	0.48
STVPh-48/STVPy-74	64	532.1/533.2	0.67	399.0/399.9	0.68
STVPh-76/STVPy-74	61	532.2/533.3	0.72	399.0/400.0	0.84

methyl styrene) (PS(OH)).³² This reflects strong self-association due to hydrogen bonding between hydroxyls of STVPh compared to those of PS(OH). In STVPh/STVPy-74-*h* blends or complexes, the O 1s peaks are shifted significantly to the low-BE side, indicating that the oxygen in the blends or complexes becomes more electronegative. Each O1s peak of STVPh/STVPy blends or complexes can be deconvoluted into two component peaks: one remains at 533.2 eV and the other is around 532.1 eV.²⁶ Generally, the fraction of the O 1s low-BE component peak increases with hydroxyl content, indicating that more hydroxyl groups can interact with pyridyl via hydrogen bonding, and that in the complexes, STVPh and STVPy chains have a larger possibility to interact with each other.

Table 3 shows the curve fitting results of N 1s and O 1s spectra of STVPh/STVPy blends. The fraction of low BE O1s peak and the fraction of high BE N1s peak all increase with VPh contents. It should be noted that even for STVPh-76/STVPy-74-*h* complexes, the fraction of low BE O1s peak and high BE N 1s peak is less than 1.0, indicating that not all of the hydroxyl groups can be hydrogen bonded to pyridyl groups. The fraction of low-BE O1s component does not agree with the high-BE N1s component for a given STVPh/STVPy blends, but if we take into consideration the surface composition, the number of hydroxyl and pyridyl groups participating in hydrogen bonding interactions agree very well.²⁵ This also confirmed the accuracy of XPS analysis and subsequent curve fitting processes.

Effect of Bulk Mixing Thermodynamics on the Surface Composition

The surface chemical composition of the blends or interpolymer complexes was calculated from

the N/C peak area ratio in the XPS spectrum, and the results are also shown in Table 2. It was found that for immiscible PS/STVPy-74-*h* and STVPh-3/STVPy-74-*h*, PS or STVPh-3 is enriched on the surface; this is reasonable since PS and STVPh-3 have much lower surface free energies compared with that of STVPy-74 (the surface free energies of PS, poly(vinyl phenol), and poly(4-vinyl pyridine) homopolymers are 40.2, 55.0, and 68.2 mJ m⁻², respectively).³³ In a previous article, we have investigated a series of STVPh random copolymers and found that there is no segregation of styrene or vinyl phenol units even at the top-most surface layer, so the surface free energy of STVPh random copolymers is presumed to increase from 40.2 to 55.0 mJ m⁻² when VPh contents increases from 0 to 100 mol %. This has also been confirmed by contact angle measurements.²⁶

The enrichment of the surface by PS or STVPh-3 can reduce the total surface free energy. For miscible STVPh-9/STVPy-74-*h* and STVPh-16/STVPy-74, the surfaces are also enriched with STVPh (see Fig. 3). But it was unexpected that the surface enrichment of STVPh in the miscible blends is higher than that in the immiscible ones, considering that the differences in surface free energies are smaller in the miscible blends compared to those in the immiscible ones. This should be due to the strong hydrogen bonded self-association between hydroxyl groups in different STVPh chains. The self-association of STVPh increases with VPh contents. Although DSC measurements show only one T_g, this only indicates miscibility on a length scale of 20–40 nm. While our XPS setup has a sampling depth of about 5 nm, it was concluded that the self-association of component polymers is also playing an important factor on the surface chemical composition.

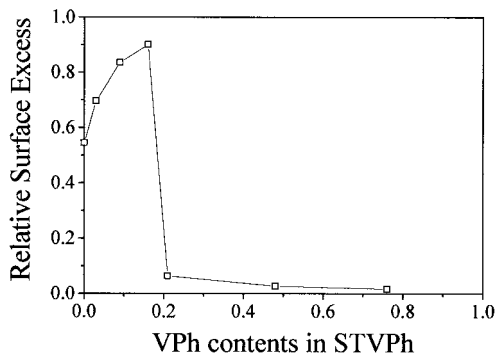


Figure 3. Ratio of surface excess, as determined by surface excess concentrations to bulk concentrations of STVPh in STVPh/STVPh blends or complexes as a function of VPh contents in STVPh.

When VPh content increased to 21 mol % and even higher, interpolymer complexes started to form. It was found that the surface excess of STVPh decreased dramatically (see Fig. 3). For STVPh-21/STVPh-74, STVPh-48/STVPh-74, and STVPh-76/STVPh-74 complexes, the surface and bulk composition are very close. This indicates that for interpolymer complexes, if the density of hydrogen bonding interaction is high enough, unlike chains are interwoven with each other, and the surface enrichment of the lower surface energy component is barely detectable, leading to nearly no differences in chemical compositions between surface and bulk. In the complexes, STVPh and STVPh form a new supramolecular species that behaves like a single pure polymer.

ToF-SIMS is a more surface sensitive technique than is XPS. The main differences between these two techniques are the information depth (1 nm and 5 nm, respectively). The ToF-SIMS spectra of STVPh²⁶ and STVPh²⁴ have previously been reported. The peak at $m/z = 93$ characteristic of VPh can distinguish VPh from styrene and VPh units. Figure 4 shows the normalized intensities of the peak at $m/z = 93$ as a function of VPh molar contents of STVPh in STVPh-STVPh-74-h blends or complexes. When the VPh content in STVPh increases from 0 to 16 mol %, the normalized intensities of the peak at $m/z = 93$ decrease to a minimum. As VPh contents increase further, the normalized intensities increase sharply and keep constant in all the interpolymer complexes. This is in good agreement with Figure 3, which shows that the surface excess of STVPh first increases and then decreases to nearly zero as the VPh contents in STVPh continue to increase. So even in the top-most 1 nm layer, the surface enrichment of

STVPh follows the same trend as that determined by XPS.

We have also studied the effect of molecular weight of STVPh-74 on the surface composition in immiscible STVPh-3/STVPh-74, miscible STVPh-9/STVPh-74 blends, and STVPh-76/STVPh-74 complexes (Table 2). Generally, surface free energies of polymers will increase with increasing molecular weight.^{13,14} For immiscible STVPh-3/STVPh blends, when the molecular weight of STVPh-74 decreased from 109×10^3 to 10×10^3 , the surface excess of STVPh-3 decreased from 35 to -2 mol %, that is, the surface even becomes STVPh rich for STVPh-3/STVPh-74-*l*. This reflects the effect of molecular weight on the surface free energy and on the surface composition of polymer blends.^{13,14} For miscible blends of STVPh-9 and STVPh-74 with different molecular weights, the effect of molecular weight of STVPh on the surface composition is much less prominent compared to immiscible STVPh-3/STVPh-74 blends. The surface excess of STVPh-9 only decreased from 42 to 29 mol %. When the blends formed interpolymer complexes, there was almost no surface enrichment by STVPh, even when STVPh-74 with the lowest molecular weight (STVPh-74-*l*) was used. This is in great contrast to immiscible and miscible polymer blends. This again confirms that in interpolymer complexes, the pairing between complementary chains can overcome the large differences in surface free energies between component polymers.

CONCLUSIONS

For immiscible and miscible STVPh/STVPh blends, surface enrichment of the lower surface

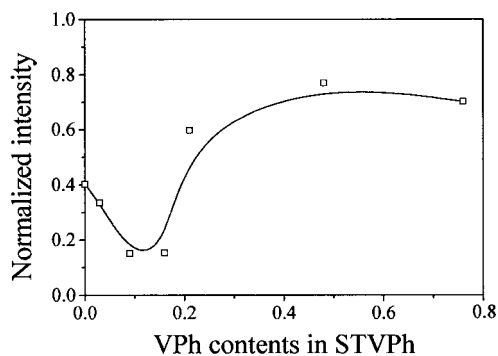


Figure 4. Normalized ToF-SIMS intensities of peaks at $m/z = 93$ as a function of VPh contents in STVPh in STVPh-STVPh-74-h blends or complexes.

energy component STVPh was always observed. Increasing VPh contents in STVPh from 0 to 16 mol % spans the immiscibility–miscibility transition and also decreased the differences in surface free energies between STVPh and STVPy, but surface enrichment of STVPh continued to increase to a maximum. In the immiscible and miscible blends, decreasing the molecular weights of STVPy systematically reduced surface enrichment of STVPh. For STVPh/STVPy complexes, surface enrichment of STVPh is barely detectable, and STVPh and STVPy form a new supramolecular species. Interpolymer complexation is now the decisive factor determining the surface composition, dominating over the surface free energy differences.

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